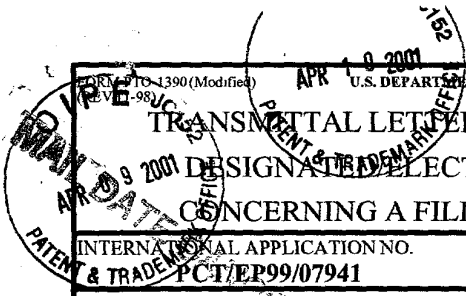


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PCT



U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>D-42992-01</b>
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) <b>09/807210</b>
INTERNATIONAL APPLICATION NO. <b>PCT/EP99/07941</b>	INTERNATIONAL FILING DATE <b>19/10/1999</b>	PRIORITY DATE CLAIMED <b>29/10/1998</b>

TITLE OF INVENTION  
**NEW HIGH RESISTANCE HEAT-SHRINKABLE THERMOPLASTIC FILM**

APPLICANT(S) FOR DO/EO/US  
**PALEARI, Mario and BUZZI, Giampaolo**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

**Items 13 to 20 below concern document(s) or information included:**

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☐ Other items or information:



**28236**

PATENT TRADEMARK OFFICE

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) <b>09/807210</b>		INTERNATIONAL APPLICATION NO. <b>PCT/EP99/07941</b>		ATTORNEY'S DOCKET NUMBER <b>D-42992-01</b>	
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21. The following fees are submitted:

BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5)) :				CALCULATIONS PTO USE ONLY	
<input type="checkbox"/>	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .....		<b>\$970.00</b>		
<input checked="" type="checkbox"/>	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO .....		<b>\$840.00</b>		
<input type="checkbox"/>	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....		<b>\$690.00</b>		
<input type="checkbox"/>	International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....		<b>\$670.00</b>		
<input type="checkbox"/>	International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) .....		<b>\$96.00</b>		
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>\$840.00</b>	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<b>\$0.00</b>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	10 - 20 =	0	x \$18.00	<b>\$0.00</b>	
Independent claims	2 - 3 =	0	x \$78.00	<b>\$0.00</b>	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$840.00</b>	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>SUBTOTAL =</b>				<b>\$840.00</b>	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				<b>\$0.00</b>	
<b>TOTAL NATIONAL FEE =</b>				<b>\$840.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				<b>\$0.00</b>	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$840.00</b>	
				<b>Amount to be: refunded</b>	\$
				<b>charged</b>	\$

☐ A check in the amount of \_\_\_\_\_ to cover the above fees is enclosed.

☒ Please charge my Deposit Account No. **07-1765** in the amount of **\$840.00** to cover the above fees.  
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **07-1765** A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

**Mark B. Quatt**  
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*Mark B. Quatt*

\_\_\_\_\_  
SIGNATURE

**Mark B. Quatt**  
\_\_\_\_\_  
NAME

**30,484**  
\_\_\_\_\_  
REGISTRATION NUMBER

**April 10, 2001**  
\_\_\_\_\_  
DATE

NEW HIGH RESISTANCE HEAT-SHRINKABLE THERMOPLASTIC FILM

The present invention refers to a multi-layer, heat-shrinkable, thermoplastic film endowed with a desirable balance of properties, including good shrink properties, good optical properties, very good mechanical properties and a peculiar sealability performance.

5 The invention also relates to containers, such as tubing, bags and pouches, made with the film.

In general terms, the packaging of food items by means of a heat-shrinkable, gas- barrier, thermoplastic film comprises configuring the heat-shrinkable packaging material, either partially or completely, around a product (e.g. by placing the food item within a bag or pouch  
10 fabricated from the film), removing excess air from inside the package (e.g. vacuumizing the bag or pouch), sealing it and thereafter exposing the package to a heat source thereby causing the heat-shrinkable film to shrink and conform with the contours of the packaged food.

These films provide to the packaged food an attractive appearance and in the mean time protect the packaged product from the environment and prolong the shelf life of the packaged product.

These films therefore need to have good gas barrier properties and mainly good sealing properties, in order to guarantee that the atmosphere within the package will not be affected by the atmosphere outside the package; they also need to have high mechanical properties to guarantee that the package will survive the handling involved in the product distribution  
20 chain; finally they also need to have good optical properties and good shrink properties to provide the end package with the attractive appearance.

Packaging films with an adequate balance of the above properties are known in the literature and spread in the market.

A problem that is however often found with the available films is that in the packaging  
25 process it is generally necessary to carefully position the packages to be vacuumized and sealed, one close to the other, in the vacuum chamber, so as to avoid any overlapping of the packages. In fact when overlapped or partially overlapped packages are heat-sealed, either it is not possible to get a seal of sufficient seal strength between the innermost heat-sealing layers

of each overlapped package or, if the temperature and pressure of the sealing bars are high enough to guarantee sealing through the overlapped webs, sealing of the overlapped outermost layers may occur, thus leading to a high number of rejects. This also means that in the packaging process the speed of the overall process is limited by the number of packages that, at each sealing cycle, can be positioned, without overlapping, in the vacuum and sealing chamber.

Using bags that can suitably be heat-sealed also when overlapping occurs, without problems of insufficient seal strength and/or sealing or sticking of the outer abuse layers, a higher number of packages could be sealed in each sealing cycle with an increase in productivity. Also, the positioning of the packages in the vacuum and sealing chamber, one along the other with no overlapping, would not be a must thus rendering the presence of an operator dedicated to said positioning, less critical.

While it is easy to list the desired properties, getting a suitable balance thereof by means of a stable and reproducible manufacturing process is not always possible.

#### SUMMARY OF THE INVENTION

We have discovered films which can provide for a combination of desirable characteristics: high impact strength, high abuse resistance, high free shrink at 90 °C, high gloss and package presentation, good sealability and seal strength, and stack/overlap sealing capability and can be manufactured via a stable and controlled process.

In a first aspect, the present invention is directed to a heat-shrinkable multi-layer film comprising at least

- a first outer heat-sealing layer (a) comprising one or more polyolefins;
- a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and
- an intermediate gas barrier layer (c) comprising PVDC.

In a second aspect the present invention is directed to a heat-shrinkable multi-layer film comprising at least

- a first outer heat-sealing layer (a) comprising one or more polyolefins;
- a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and

an intermediate gas barrier layer (c) comprising PVDC,  
in the form of a seamless tube with outer heat-sealing layer (a) being the innermost layer  
of the tube.

In a third aspect the present invention is directed to a container obtained from a heat-  
shrinkable multi-layer film comprising at least

a first outer heat-sealing layer (a) comprising one or more polyolefins;  
a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and  
an intermediate gas barrier layer (c) comprising PVDC,  
by a welding that involves the heat-sealing outer layer (a).

In a fourth aspect the present invention is directed to a process of manufacture of a heat-  
shrinkable multi-layer film comprising at least

a first outer heat-sealing layer (a) comprising one or more polyolefins;  
a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and  
an intermediate gas barrier layer (c) comprising PVDC,

that comprises (co)-extrusion of at least the first outer heat-sealing layer (a) and possibly  
of other but not all the layers of the overall structure in the desired sequence, to give a first  
extrudate; extrusion coating of the obtained first extrudate with the remaining layers of the  
overall structure in the desired sequence, to give a second extrudate; and orientation thereof.

#### DEFINITIONS

In this specification and the accompanying claims:

the term "film" refers to a flat or tubular flexible structure of thermoplastic material having  
a thickness up to about 150  $\mu\text{m}$ ;

the term "heat-shrinkable" refers to a film that shrinks by at least 10 % of its original  
dimensions, in at least one of the longitudinal and transverse directions, when heated to 90 °C  
for 4 seconds;

the phrase "longitudinal direction" or " machine direction", herein abbreviated "MD",  
refers to a direction "along the length" of the film, i.e., in the direction of the film as the film  
is formed during extrusion and/or coating;

the phrase "transverse direction", herein abbreviated "TD", refers to a direction across the film, perpendicular to the machine direction;

the phrase "outer layer" refers to any film layer having only one of its principal surfaces directly adhered to another layer of the film;

5 the phrases "sealing-layer", "heat-sealable layer" and "heat sealing layer", refer to the outer film layer involved in the sealing of the film to itself, to another film, and/or to another article which is not a film;

the phrase "abuse layer" and "abuse-resistant layer" refer to the outside layer of the film which is not the sealant layer and which is subject to abuse;

10 the phrases "inner layer", "intermediate layer", and "internal layer" refer to any film layer having both of its principal surfaces directly adhered to another layer of the film;

the phrase "tie layer" refers to any internal layer having the primary purpose of adhering two layers to one another;

15 the term "core", and the phrase "core layer" refer to any internal layer which preferably has a function other than serving as a tie or compatibilizer for adhering two layers to one another;

the phrase "directly adhered", as applied to film layers, is defined as adhesion of the subject film layer to the object film layer, without a tie layer, adhesive, or other layer there-between. In contrast, as used herein, the word "between", as applied to a film layer, expressed as being between two other specific layers, includes both direct adherence of the subject layer  
20 to the two other layers it is between, as well as a lack of direct adherence to either or both of the two other layers the subject layer is between, i.e., one or more additional layers can be imposed between the subject layer and one or more of the layers the subject layer is between.

As used herein, the term "homopolymer" is used with reference to a polymer resulting from the polymerization of a single monomer, i.e., a polymer consisting essentially of a single  
25 type of repeating unit.

As used herein, the term "copolymer" refers to polymers formed by the polymerization reaction of at least two different monomers.

As used herein, the term "polymer" refers to both homo-polymers and co-polymers as defined above.

As used herein the term "polyolefin" is used with reference to any thermoplastic polymer of simple olefins such as ethylene, propylene, and butene, and co-polymer comprising a major proportion of a simple olefin and a minor proportion of one or more comonomers copolymerisable therewith such as typically another olefin, vinyl acetate, alkyl (meth)acrylate, (meth)acrylic acid, maleic anhydride, and the like, as well as modifications thereof. The term "polyolefin" specifically includes polyethylene, ethylene co-and ter-polymers, polybutene, propylene-butene co-polymer, and the like.

As used herein the terms "polyethylene" and "ethylene homopolymer" identify polymers consisting essentially of an ethylene repeating unit. Depending on the polymerization process employed, polymers with a different degree of branching and a different density can be obtained. Those characterized by a low degree of branching and showing a density higher than  $0.940 \text{ g/cm}^3$  are called HDPE while those with a higher level of branching and a density up to  $0.940 \text{ g/cm}^3$  are called LDPE.

As used herein the term "ethylene copolymer" refers to the copolymers of ethylene with one or more other olefins and/or with a non-olefinic comonomer copolymerizable with ethylene, such as vinyl monomers, modified polymers thereof, and the like. Specific examples include ethylene/ $\alpha$ -olefin copolymers, ethylene/vinyl acetate copolymers, ethylene/ethyl acrylate copolymers, ethylene/butyl acrylate copolymers, ethylene/methyl acrylate copolymers, ethylene/acrylic acid copolymers, ethylene/methacrylic acid copolymers, ionomer resins, ethylene/alkyl acrylate/maleic anhydride ter-polymers, etc..

As used herein, the phrase "heterogeneous polymer" refers to polymerization reaction products of relatively wide variation in molecular weight and relatively wide variation in composition distribution, i.e., polymers made, for example, using conventional Ziegler-Natta catalysts. Such polymers typically contain a relatively wide variety of chain lengths and comonomer percentages.

As used herein, the phrase "homogeneous polymer" refers to polymerization reaction products of relatively narrow molecular weight distribution and relatively narrow composition distribution. Homogeneous polymers exhibit a relatively even sequencing of comonomers within a chain, the mirroring of sequence distribution in all chains, and the similarity of length of all chains, and are typically prepared using metallocene, or other single-site type catalysis.

More particularly, homogeneous ethylene/ $\alpha$ -olefin copolymers may be characterized by one or more methods known to those of skill in the art, such as molecular weight distribution (Mw/Mn), composition distribution breadth index (CDBI), and narrow melting point range and single melt point behavior.

A homogeneous ethylene/ $\alpha$ -olefin copolymer can, in general, be prepared by the copolymerization of ethylene and any one or more  $\alpha$ -olefin. Preferably, the  $\alpha$ -olefin is a C<sub>3</sub>-C<sub>20</sub>  $\alpha$ -mono-olefin, more preferably, a C<sub>4</sub>-C<sub>12</sub>  $\alpha$ -mono-olefin, still more preferably, a C<sub>4</sub>-C<sub>8</sub>  $\alpha$ -mono-olefin. Still more preferably, the  $\alpha$ -olefin comprises at least one member selected from the group consisting of butene-1, hexene-1, and octene-1. Most preferably, the  $\alpha$ -olefin comprises octene-1, and/or a blend of hexene-1 and butene-1.

Processes for preparing homogeneous polymers are disclosed in US Patent No. 5,206,075, US Patent No. 5,241,031, and PCT International Application WO 93/03093. Further details regarding the production and use of one genus of homogeneous ethylene/ $\alpha$ -olefin copolymers are disclosed in US Patent No. 5,206,075, to Hodgson, Jr.; US Patent No. 5,241,031, to Mehta; PCT International Publication Number WO 93/03093, in the name of Exxon Chemical Company; and PCT International Publication Number WO 90/03414, in the name of Exxon Chemical Patents, Inc.. Still another genus of homogeneous ethylene/ $\alpha$ -olefin copolymers is disclosed in US Patent No. 5,272,236, to Lai, et.al., and US Patent No. 5,278,272, to Lai, et.al..

As used herein, the phrase "ethylene/ $\alpha$ -olefin copolymers", "ethylene/ $\alpha$ -olefin copolymers", refer to such heterogeneous materials as linear low density polyethylene (LLDPE), linear medium density polyethylene (LMDPE) and very low and ultra low density polyethylene (VLDPE and ULDPE); and homogeneous polymers such as metallocene



catalyzed polymers such as EXACT™ materials supplied by Exxon, AFFINITY™ and ENGAGE™ materials supplied by Dow, LUFLEXEN™ materials supplied by BASF and TAFMER™ materials supplied by Mitsui Petrochemical Corporation. These materials generally include copolymers of ethylene with one or more comonomers selected from C4 to C10  $\alpha$ -olefins such as butene-1, hexene-1, octene-1, etc..

As used herein the term "modified polyolefin" is inclusive of modified polymer prepared by copolymerizing the homopolymer of the olefin or copolymer thereof with an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like; as well as of modified polymer obtained by incorporating, into the olefin homopolymer or copolymer, an unsaturated carboxylic acid, e.g. maleic acid, fumaric acid, or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like. Examples of said modified polyolefins are graft copolymers of maleic acid or anhydride onto ethylene/ $\alpha$ -olefin copolymers, graft copolymers of fused ring carboxylic anhydrides onto polyethylene, resin mixtures of these and mixtures with polyethylene or ethylene/ $\alpha$ -olefin copolymers.

As used herein the term "ethylene-acrylic acid and ethylene-methacrylic acid copolymers" refers to copolymers of ethylene with a copolymerisable ethylenically unsaturated carboxylic acidic monomer selected from acrylic acid and methacrylic acid. The copolymer typically contains from about 4 to about 18% by weight of acrylic or methacrylic acid units. Said copolymer can also contain, copolymerised therein an alkyl (meth)acrylate, such as n-butyl acrylate or methacrylate or isobutyl acrylate or methacrylate. Said copolymer can be in the free acid form as well as in the ionized or partially ionized form wherein the neutralizing cation can be any suitable metal ion, e.g. an alkali metal ion, a zinc ion or other multivalent metal ions; in this latter case the copolymer is also termed "ionomer".

As used herein the term "ethylene-vinyl acetate copolymer" or "EVA" is intended to refer to a copolymer formed from ethylene and vinyl acetate monomers wherein the ethylene derived units in the copolymer are present in major amounts; preferably between about 60 %

and 98 % by weight and the vinyl acetate derived units in the copolymer are present in minor amounts, preferably between about 2 % and about 40 % by weight.

As used herein the term "ethylene-alkyl (meth)acrylate copolymers" refers to copolymers of ethylene with alkyl (meth)acrylates, e.g. methyl (meth)acrylate, butyl (meth)acrylate, and iso-butyl (meth)acrylate wherein the ethylene derived units in the copolymer are present in major amounts and the alkyl (meth)acrylate derived units in the copolymer are present in minor amounts, preferably between about 2 % and about 28 % by weight.

As used herein the term EVOH refers to saponified products of ethylene-vinyl ester copolymers, generally of ethylene-vinyl acetate copolymers, wherein the ethylene content is typically comprised between 20 and 60 % by mole and the degree of saponification is generally higher than 85 % preferably higher than 95 %.

As used herein the term PVDC refers to a vinylidene chloride copolymer wherein a major amount of the copolymer comprises vinylidene chloride and a minor amount of the copolymer comprises one or more unsaturated monomers copolymerisable therewith, typically vinyl chloride, and alkyl acrylates or methacrylates (e.g. methyl acrylate or methacrylate) or to a blend thereof in different proportions. Generally said PVDC contains plasticisers and/or stabilizers as known in the art.

As used herein, the term polyamide is intended to refer to both polyamides and copolyamides. This term specifically includes those aliphatic polyamides or copolyamides commonly referred to as e.g. polyamide 6 (homopolymer based on  $\epsilon$ -caprolactam), polyamide 69 (homopolycondensate based on hexamethylene diamine and azelaic acid), polyamide 610 (homopolycondensate based on hexamethylene diamine and sebacic acid), polyamide 612 (homopolycondensate based on hexamethylene diamine and dodecandioic acid), polyamide 11 (homopolymer based on 11-aminoundecanoic acid), polyamide 12 (homopolymer based on  $\omega$ -aminododecanoic acid or on laurilactam), polyamide 6/12 (polyamide copolymer based on  $\epsilon$ -caprolactam and laurilactam), polyamide 6/66 (polyamide copolymer based on  $\epsilon$ -caprolactam and hexamethylenediamine and adipic acid), polyamide 66/610 (polyamide copolymers based on hexamethylenediamine, adipic acid and sebacic

acid), modifications thereof and blends thereof. Said term also includes crystalline or partially crystalline, aromatic or partially aromatic, polyamides.

Melting information by DSC are reported as second heating data, i.e., the sample is heated at a programmed rate of 10 °C/min to a temperature below its critical range, cooled down and then reheated (2<sup>nd</sup> heating) still at a programmed rate of 10 °C/min.

#### DETAILED DESCRIPTION OF THE INVENTION

A first object of the present invention is a heat-shrinkable film comprising at least the following layers:

- a first outer heat-sealing layer (a) comprising one or more polyolefins;
- a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and
- an intermediate gas barrier layer (c) comprising PVDC.

In the film according to the present invention the heat-sealing layer (a) may comprise a single polymer or a blend of two or more polymers as known in the art. Preferably the melting point of the polyolefin resin(s) of the heat-sealing layer (a) will be  $< 140$  °C, and preferably  $< 130$  °C. In a more preferred embodiment it will be comprised between about 80°C and about 128 °C.

Such a layer may for example comprise heterogeneous or homogeneous ethylene- ( $C_4$ - $C_8$ )- $\alpha$ -olefin copolymers having a density  $\leq 0.915$  g/cm<sup>3</sup>; blends thereof with minor amount of polyethylene homopolymers; ethylene-vinyl acetate copolymers; ethylene-acrylic or methacrylic acid copolymers including ionomers; blends of heterogeneous or homogeneous ethylene- ( $C_4$ - $C_8$ )- $\alpha$ -olefin copolymers having a density from about 0.915 g/cm<sup>3</sup> to about 0.930 g/cm<sup>3</sup> with ethylene-vinyl acetate copolymers or ethylene-alkyl (meth)acrylate copolymers; ethylene-propylene-butene ter-polymers; ethylene-alkyl acrylate-maleic anhydride ter-polymers; and the like polymers.

In a preferred embodiment of the present invention the heat-sealing layer (a) will comprise a heterogeneous or homogeneous ethylene- ( $C_4$ - $C_8$ )- $\alpha$ -olefin copolymer having a density  $\leq 0.915$  g/cm<sup>3</sup>, and even more preferably a heterogeneous or homogeneous ethylene- ( $C_4$ - $C_8$ )- $\alpha$ -olefin copolymer having a density comprised between about 0.895 g/cm<sup>3</sup> and about 0.912

g/cm<sup>3</sup>. The Melt Index of said heterogeneous or homogeneous ethylene-(C<sub>4</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymer may range from about 0.1 to about 15 g/10' (measured by ASTM D-1238, Condition E). However, preferred values are in the range 0.5-10 g/10' and still more preferred values are in the range 1.0-7.0 g/10'.

5 The resins used in the manufacture of the films according to the present invention, not only in the heat-sealing (a) but also in the outer abuse layer (b) or in any of the intermediate layers, can be suitably additivated as known in the art in order to improve the properties of the film or the manufacturing process thereof.

As an example the resins may contain stabilizers, anti oxidants, pigments, UV absorbers, cross-linking enhancers or cross-linking inhibitors, anti-fog agents, slip and anti-blocking agents, etc., as conventionally used in this field.

10 The polyamide of the outer layer (b) will have a melting point  $\geq 175$  °C, typically of from about 175 °C to about 250°C; preferably of from about 180 °C to about 240 °C; more preferably of from about 185 °C to about 230 °C; and still more preferably of from about 188 °C to about 225 °C.

15 A most preferred group of polyamides, with a melting temperature of from about 188 °C to about 225 °C, suitable for use in the outer abuse layer (b), includes certain copolyamides 6/12, such as PA6/12 CR-8 and CR-9 marketed by EMS, polyamide 66, copolyamides 6/66 such as CA95WP marketed by Allied Signal, certain polyamide 6 copolymers (modified polyamide 6) comprising less than 5 %, preferably less than 4 %, and even more preferably less than 3 % by weight of an aromatic co-monomer such as terephthalic acid, such as Sniamid™ F36T/S marketed by Caffaro, certain copolyamides of polyamide 6 and a partially aromatic polyamide, such as Durethan™ CI31F and CI31FKS marketed by Bayer, and certain terpolyamides such as those based on polyamide 6, polyamide 11, and polyamide 66, sold by 20 Bayer under the trade name Durethan™ VP KU 2-2153 or KU 2-2153F.

Preferably the outer abuse layer (b) will comprise polyamide 6, a modified polyamide 6, a co-polyamide of polyamide 6 and a partially aromatic polyamide, or a ter-polyamide based on polyamide 6, polyamide 11, and polyamide 66.

The outer abuse layer (b) will contain at least 50 % by weight and preferably at least 60 % by weight of one or more polyamides with a m.p.  $\geq 175$  °C.

In a preferred embodiment of the present invention the outer abuse layer (b) will comprise a blend comprising a polyamide having a m.p.  $\geq 175$  °C and an ethylene-vinyl alcohol copolymer. Preferred EVOH copolymers for use in such a blend will contain between about 30 and about 50 % by mole of ethylene.

When a blend with EVOH is employed for the outer abuse layer (b), the amount by weight of EVOH in said outer layer will be up to about 40 % with respect to the overall weight of the layer. Typically the amount of EVOH will be comprised between about 3 and about 40 % by weight, preferably between about 5 and about 35 % by weight, and even more preferably between about 10 and about 30 % by weight.

It has been found in fact that the presence of an amount of at least about 3 % by weight of EVOH in said outer abuse layer (b) improves stretchability of the tape, thus facilitating the orientation step and increasing the free shrink of the end structure, while it has also been found that the good mechanical properties and the stack/overlap sealing capability of the end film are maintained even when amounts as high as about 40 % by weight of EVOH are employed in said outer abuse layer (b).

The film according to the present invention requires the presence of an intermediate gas barrier layer (c) wherein said gas (e.g. oxygen, nitrogen, carbon dioxide, etc.) barrier layer comprises PVDC.

In an even more preferred embodiment the PVDC comprises vinylidene chloride-methyl acrylate copolymer, or vinylidene chloride-methyl methacrylate copolymer, or a blend of vinylidene chloride-vinyl chloride copolymer and a minor proportion of vinylidene chloride-methyl acrylate copolymer.

The thickness of the intermediate gas barrier layer (c) will generally be comprised between about 2 and about 15  $\mu\text{m}$ , as thicker gas barrier layers will not bring about any appreciable increase in barrier properties worth the additional costs involved, while thinner gas barrier layers cannot guarantee the desired low level of gas permeability. Preferably the

thickness of the intermediate gas barrier layer (c) will be comprised between about 3 and about 12  $\mu\text{m}$ , and even more preferably between about 4 and about 10  $\mu\text{m}$ .

The thickness of the outer abuse layer (b) will be typically comprised between about 2 and about 15  $\mu\text{m}$ , whereas a preferred thickness will be comprised between about 3 and about 10  $\mu\text{m}$ , and an even more preferred thickness will be comprised between about 4 and about 8  $\mu\text{m}$ . The outer abuse layer (b) needs in fact to be thick enough to provide for the desired good mechanical properties and the stack/overlap sealability, while it should not be too thick as otherwise stretchability of the tape and, as a consequence thereof, free shrink of the end structure, will be negatively affected.

The thickness of the outer heat-sealing layer (a) typically depends on the overall thickness of the film and on the number of layers present in the end structure. In case of thin films it generally ranges from about 2  $\mu\text{m}$  to e.g. about 6, or 8, or 10  $\mu\text{m}$ . In case of thicker films, such as those used for the manufacture of bags or pouches, it is typically greater than 4  $\mu\text{m}$ , preferably greater than 5  $\mu\text{m}$ , and even more preferably greater than 6  $\mu\text{m}$ , and up to about 20, 30, 40  $\mu\text{m}$  or even more.

Generally, the film has a total thickness of from about 12 to about 150  $\mu\text{m}$ ; preferably, from about 15 to about 130  $\mu\text{m}$ ; more preferably, from about 20 to about 120  $\mu\text{m}$ ; still more preferably, from about 30 to about 100  $\mu\text{m}$ ; yet still more preferably, from about 35 to about 90  $\mu\text{m}$ .

Additional inner layers can be added e.g. to increase the bulk of the overall structure and/or further improve the shrink and/or the mechanical properties of the film, etc. as known in the art.

Suitable resins for said additional intermediate layers include for instance ethylene copolymers, particularly ethylene-vinyl acetate copolymers, ethylene-alkyl acrylate or ethylene-alkyl methacrylate copolymers, ionomers, ethylene- $\alpha$ -olefin copolymers with a low density or very low density, and the like resins.

To improve the adhesion between the gas barrier layer (c) and the outer layers (a) and (b), or between the different layers, in case additional inner layers are present, tie layers can be

employed. Tie layers typically comprise a modified polyolefin or preferably a blend of a modified polyolefin with a polyolefin, such as for instance a blend of an acid or anhydride modified EVA with EVA or LLDPE. Their thickness is typically of few  $\mu\text{m}$  as their aim is just to increase the bond between the different layers.

5 In one embodiment of the present invention the film has at least four layers wherein a tie layer (d) is adhered to one of the surfaces of the gas barrier intermediate layer (c), and to either one of the outer abuse layer (c) and the outer heat-sealing layer (a). In particular, in the case of a four layer film, a tie layer (d) is generally required for bonding layer (c) to the outer abuse layer (b), while a direct adhesion between said PVDC comprising gas barrier layer (c) and the heat-sealing layer (a) may be achieved by suitably selecting the resin or the resin  
10 blend of the heat-sealing layer (a). As an example, direct adhesion between the PVDC comprising gas barrier layer (c) and the heat-sealing layer (a) can be obtained using, for the heat-sealing layer (a), ethylene-vinyl acetate copolymers, ethylene-alkyl acrylate copolymers, ethylene-alkyl methacrylate copolymers, ethylene- $\alpha$ -olefin copolymers, and the like polymers and blends thereof.  
15

In another embodiment the film has at least five layers wherein a tie layer (d) is between the sealing layer (a) and one of the surfaces of the intermediate gas barrier layer (c), and another tie layer (d'), that may be equal to or different from (d) is between the other surface of the intermediate gas-barrier layer (c) and the outer abuse layer (b).

20 The films according to the present invention can be manufactured by the so-called trapped-bubble process, which is a widely known process typically used for the manufacture of the heat-shrinkable films for food contact packaging.

According to said process, the multi-layer film is co-extruded through a round die to obtain a tube of molten polymer which is quenched immediately after extrusion without being  
25 expanded, then heated to a temperature which is above the  $T_g$  of all the resins employed and below the melting temperature of at least one of said resins, typically by passing it through a hot water bath, but alternatively using a hot air tunnel or an I.R. oven, and expanded, still at this temperature by internal air pressure to get the transversal orientation and by a differential

speed of the pinch rolls which hold the thus obtained "trapped bubble" to provide the longitudinal orientation. The film is then rapidly cooled to somehow freeze the molecules of the film in their oriented state and wound.

While in a preferred embodiment of the present invention the film is biaxially oriented and will therefore be heat-shrinkable in both directions, mono-oriented films or preferentially oriented films can be obtained by avoiding or controlling transversal or longitudinal orientation. Suitable orientation ratios are typically comprised between 2 : 1 and 5 : 1, and are preferably comprised between 2.5 : 1 and 4 : 1. Higher orientation ratios can be applied when different technologies (e.g. tenter frame) are employed for the orientation or in case of mono-axially oriented films.

As used herein, the phrase "free shrink" refers to the percent dimensional change in a 10 cm x 10 cm specimen of film, when subjected to selected heat (i.e., at a certain temperature), with the quantitative determination being carried out according to ASTM D 2732, as set forth in the 1990 Annual Book of ASTM Standards, Vol. 08.02, pp.368-371, which is hereby incorporated, in its entirety, by reference thereto.

The multi-layer film according to the present invention typically has a total free shrink of at least 20 % at 90 °C, preferably of at least 30 % at 90 °C, more preferably of at least 40 % at 90 °C and even more preferably of at least 50 % at 90 °C. "Total free shrink" is determined by summing the percent free shrink in the machine direction with the percentage of free shrink in the transverse direction. For example, a film that exhibits, at 90 °C, 20 % free shrink in the transverse direction and 20 % free shrink in the machine direction, has a "total free shrink" at 90 °C of 40 %. Unless specified otherwise, the phrase "free shrink", as used herein, refers to total free shrink.

Depending on the number of layers in the structure it may be advisable or necessary to split the co-extrusion step : in such a case a tube is first formed of a limited number of layers, with the heat-sealing layer (a) on the inside of the tube; this tube is quenched quickly and, before submitting it to the orientation step, it is extrusion-coated with the remaining layers, again



quenched quickly and then passed to the orientation. During the extrusion-coating step the tube is slightly inflated just to keep it in the form of a tube and avoid that it collapses.

The coating step can be simultaneous, by coextruding all the remaining layers altogether, so as to simultaneously adhere all of them, one over the other, to the quenched tube obtained in the first extrusion step, or this coating step can be repeated as many times as the layers which are to be added.

According to a preferred embodiment of the present invention the film is partially or wholly cross-linked. Cross-linking may be achieved either by irradiation or chemically. Preferably cross-linking is achieved by irradiation that involves submitting the film to a suitable radiation dosage of high-energy electrons, preferably using an electron accelerator, with the dosage level being determined by standard dosimetry methods. A suitable radiation dosage of high-energy electrons is in the range of up to about 120 kGy, more preferably from about 16 to about 100 kGy, and still more preferably from about 20 to about 90 kGy.

The radiation is not limited to electrons from an accelerator since any ionizing radiation may be used.

Irradiation is most preferably performed prior to orientation, on the extruded primary tape, but it could also be performed after orientation on the end film or during orientation.

If only some of the layers of the film need to be irradiated, the extrusion coating technique is used and the irradiation step is carried out on the primary tube or sheet, before extrusion coating and orientation.

In a preferred embodiment of the invention, the film is obtained by extrusion coating and only the primary tape, that will not comprise the PVDC layer, is irradiatively cross-linked.

Particularly when the whole film is cross-linked by irradiation, it may be advantageous to make use of cross-linking controlling agents which can be added to the different layers in different amounts to control the degree of cross-linking in each layer. Suitable cross-linking controlling agents are for instance those described in EP-A-333,294.

Alternatively, chemical cross-linking of the resins can be achieved by the addition of suitable cross-linking agents, e.g. peroxides, to the resins to be cross-linked.

It is also possible to combine chemical cross-linking and irradiation, as an example when the cross-linking agents added to the resins need some irradiation to trigger the cross-linking reaction.

The films according to the present invention may optionally be subjected to other types of energetic radiation treatments that may have different aims. As an example the outer abuse layer (b) of the film may be subjected to a corona discharge treatment to improve the print receptivity characteristics of the film surface or the outer heat-sealant layer (a) may be subjected to a corona discharge treatment to improve the heat-sealability and/or the meat adhesion properties thereof.

In some instances it may be desirable to submit the oriented structure to an annealing step; this typically consists in a controlled heating-cooling treatment that is carried out on the oriented film in order to have better control on low temperature dimensional stability of the heat-shrinkable film while maintaining the shrink properties at higher temperatures.

The film of the present invention may be used either as a film, or as a bag or pouch, or as a tubing to form a package in a conventional manner.

In a preferred embodiment the heat-shrinkable film of the present invention is obtained as a seamless tubular film wherein the heat-sealing layer (a) is the innermost layer of the tube and the outer abuse layer (b) is the outermost layer of the tube and, if desired, individual bags are formed by transverse sealing and cutting across the flattened tubular film.

In a second aspect, therefore, the present invention is directed to a heat-shrinkable multi-layer film comprising at least

- a first outer heat-sealing layer (a) comprising one or more polyolefins;
- a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and
- an intermediate gas barrier layer (c) comprising PVDC,

in the form of a seamless tube with outer heat-sealing layer (a) being the innermost layer of the tube.

Alternatively the film may also be prepared by flat extrusion (co-extrusion or extrusion coating) followed by orientation in one or both directions via tenter frame. Orientation may be

carried out in such a case either sequentially or simultaneously. The flat film can then be converted to transverse sealed (TS) bags or pouches, by center-folding the film and then transversely sealing and severing it. Other methods of making bags and packages are known and may be readily adapted to use with the multi-layer films of the invention. Preferably, the bag is produced by sealing the outer heat-sealing layer (a) to itself, whereby said outer layer is an inside bag layer and the outer abuse layer (b) is an outside bag layer.

In a third aspect the present invention is directed to a container obtained from a heat-shrinkable multi-layer film comprising at least

a first outer heat-sealing layer (a) comprising one or more polyolefins;

a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and

an intermediate gas barrier layer (c) comprising PVDC,

by a welding involving the outer heat-sealing layer (a), whereby said outer layer (a) is the inside bag layer and the outer abuse layer (b) is the outside bag layer.

The present invention will now be described in more detail with particular reference to the following Examples:

#### Example 1

A seven-layer film has been prepared by extrusion coating through a round die.

A substrate formed of the following layers (a)/(e)/(f)/(g), wherein the heat-sealing layer (a) is the innermost layer of the tube, has been co-extruded, quickly quenched with a water cascade, irradiated at a dosage level of 64 kGy and coated with the sequence of three layers, (c)/(d)/(b), wherein the outer abuse layer (b) is the outermost layer of the overall tube. The extrusion coated tape has then been quenched, re-heated by passing it through a water bath at about 95 °C-98 °C, and oriented at this temperature (with orientation ratios of about 3.6 : 1 in the longitudinal direction and about 3.2 : 1 in the transverse direction) by the trapped-bubble process.

The sequence of layers (from the innermost heat-sealing layer (a) to the outermost abuse layer (b)) in the overall structure is as follows:

(a)/(e)/(f)/(g)/(c)/(d)/(b)

wherein the resins used for the different layers and, between parentheses, the thickness of each layer are reported below:

(a) homogeneous ethylene-octene-1 copolymer -  $d = 0.905 \text{ g/cm}^3$  - m.p. =  $99^\circ\text{C}$  (DSC - 2<sup>nd</sup> heating) - MI = 6 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) -

5 Affinity PL 1280 by Dow ( $9 \mu\text{m}$ )

(e) a blend of 70 % by weight of ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) - Escorene Ultra FI00014 by Exxon] and 30 % by weight of heterogeneous ethylene-octene-1 copolymer [ $d = 0.920 \text{ g/cm}^3$  - m.p. =  $124^\circ\text{C}$  (DSC - 2<sup>nd</sup> heating) - MI = 1 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) - Dowlex 2045 E by Dow] ( $6 \mu\text{m}$ )

(f) a blend of 20 % by weight of ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) - Escorene Ultra FI00014 by Exxon] and 80 % by weight of heterogeneous ethylene-octene-1 copolymer [ $d = 0.920 \text{ g/cm}^3$  - m.p. =  $124^\circ\text{C}$  (DSC - 2<sup>nd</sup> heating) - MI = 1 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) - Dowlex 2045 E by Dow] ( $7 \mu\text{m}$ )

(g) a blend of 70 % by weight of ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) - Escorene Ultra FI00014 by Exxon] and 30 % by weight of heterogeneous ethylene-octene-1 copolymer [ $d = 0.920 \text{ g/cm}^3$  - m.p. =  $124^\circ\text{C}$  (DSC - 2<sup>nd</sup> heating) - MI = 1 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) - Dowlex 2045 E by Dow] ( $8 \mu\text{m}$ )

(c) a blend of 30 % by weight of vinylidene chloride-methyl acrylate copolymer, 68 % by weight of vinylidene chloride-vinyl chloride and 2 % by weight of epoxidised soybean oil ( $6 \mu\text{m}$ )

(d) anhydride grafted and rubber modified LLDPE - Tymor 1203 by Morton ( $4 \mu\text{m}$ )

(b) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a terpolyamide based on polyamide 6, polyamide 11, and polyamide 66 [sold by Bayer under the trade name Durethan® VP KU 2-2153 (m.p.  $191^\circ\text{C}$ )] ( $6 \mu\text{m}$ ).

## Example 2

A seven layer film has been obtained by following substantially the same procedure described in the foregoing example but replacing the resins used for layers (e), (f), and (g), with the following ones :

5 (e') ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Escorene Ultra FI00014 by Exxon]

(f') ethylene-methacrylic acid copolymer [12 % MA, MI = 1.6 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Nucrel 1202 by DuPont]

10 (g') ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Escorene Ultra FI00014 by Exxon]

## Example 3

A seven-layer film has been obtained by following substantially the same procedure described in Example 1 but replacing the blend used in layer (b) with the following one :

15 (b') blend of 15 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 85 % by weight of a polyamide 6/66 with m.p. 196 °C [marketed by Allied Signal as CA95WP].

## Example 4

A five-layer film has been prepared by extrusion coating through a round die.

20 A substrate formed of the following two layers (a')/(e''), wherein the heat-sealing layer (a) is the innermost layer of the tube, has been co-extruded, quickly quenched with a water cascade, irradiated at a dosage level of 64 kGy and coated with the sequence of three layers, (c)/(d)/(b), wherein the outer abuse layer (b) is the outermost layer of the overall tube. The extrusion-coated tape has then been quenched, re-heated by passing it through a water bath at about 95 °C-98 °C, and oriented at this temperature by the trapped-bubble process.

25 The sequence of layers (from the innermost heat-sealing layer (a) to the outermost abuse layer (b)) in the overall structure is as follows:

(a')/(e'')/(c)/(d)/(b)

wherein the resins used for the layers and, between parentheses, the thickness of each layer are reported below:

(a') heterogeneous ethylene-octene-1 copolymer [ $d = 0.911 \text{ g/cm}^3$  -  $MI = 7 \text{ g/10'}$  (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) - Stamylex 08-076 by DSM] (14  $\mu\text{m}$ )

(e'') ethylene-vinyl acetate copolymer [9 % VA,  $MI = 3.0 \text{ g/10'}$  (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) - Evatane 1020 VN 3 by Elf Atochem] (20  $\mu\text{m}$ )

(c), (d), and (b) have the same composition as in Example 1 and a thickness of about 5  $\mu\text{m}$  each.

#### Example 5

A five layer film has been prepared by following essentially the same procedure as in the foregoing Example 4 but replacing in the outermost layer the blend (b) with the blend (b') described in Example 3.

#### Example 6

A seven layer film has been obtained by following substantially the same procedure as in Example 2 but replacing in the outermost layer the blend (b) with the blend (b') described in Example 3 and modifying the thickness of the layers.

In the overall structure (a)/(e')/(f')/(g')/(c)/(d)/(b') the thickness of each layer is, expressed in  $\mu\text{m}$ , 13/6/6/7//5/9/3.

#### Example 7

A five-layer film has been prepared by following substantially the same procedure described in Example 4 but replacing the blend used in the outermost layer with the following one :

(b'') blend of 25 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 75 % by weight of polyamide 6 copolymer (polycaprolactam containing about 1 % terephthalic acid comonomer) with m.p. = 213°C (DSC - 2<sup>nd</sup> heating) - [Sniamid F36T/S by Caffaro].

#### Example 8

A five-layer film has been prepared essentially as described in Example 4 but replacing the blend used for the outer abuse layer (b) with

(b''') blend of 10 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 90 % by weight of co-polyamide 6/6I with m.p. = 188-190 °C (DSC - 2<sup>nd</sup> heating) [Durethan™ CI31F by Bayer].

#### Examples 9 and 10

Two seven layer films have been prepared essentially as described in Example 1 but adding to the blend used for the outer abuse layer (b), 4 wt. % of a masterbatch of slip and antiblocking agents in a polyamide 6/12 copolymer with m.p. ≈ 190 °C (Grilon 3476FS by ESM - Example 9) or in a polyamide 6/12 copolymer with m.p. ≈ 135 °C (Grilon 7361FS by EMS - Example 10).

#### Example 11

A seven-layer film is prepared essentially as described in Example 1 but replacing the blend used for the outer abuse layer (b) with

(b<sup>iv</sup>) a ternary copolyamide based on polyamide 6, polyamide 11, and polyamide 66 with m.p. = 191 °C (DSC- 2<sup>nd</sup> heating) - [Durethan™ VP KU 2-2153 by Bayer].

#### Example 12

A seven-layer film is prepared essentially as described in Example 1 but replacing the blend used for the outer abuse layer (b) with

(b<sup>v</sup>) a co-polyamide 6/12 with m.p. = 190 °C ((DSC- 2<sup>nd</sup> heating) [CR-8 by EMS].

#### Example 13

A seven-layer film is prepared essentially as described in Example 1 but replacing the blend used for the outer abuse layer (b) with

(b<sup>vi</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a co-polyamide 6/12 with m.p. = 190 °C ((DSC- 2<sup>nd</sup> heating) [CR-8 by EMS].

#### Example 14

A seven-layer film is prepared essentially as described in Example 1 but replacing the resin used for layer (d) with

(d') a modified VLDPE resin sold by Mitsui as Admer AT 1094E.

#### Example 15

A seven-layer film is prepared essentially as described in Example 1 but replacing the blend used for the outer abuse layer (b) with

(b<sup>vi</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of co-polyamide 6/6I with m.p. = 188-190 °C (DSC - 2<sup>nd</sup> heating) [Durethan™ CI31F by Bayer].

#### Example 16

A seven-layer film is prepared by following essentially the same procedure of Example 1.

A substrate formed of the following layers (a')/(e')/(f')/(g'), wherein the heat-sealing layer (a') is the innermost layer of the tube, has been co-extruded, quickly quenched with a water cascade, irradiated at a dosage level of 64 kGy and coated with the sequence of three layers, (c)/(d')/(b<sup>iv</sup>), wherein the outer abuse layer (b<sup>iv</sup>) is the outermost layer of the overall tube. The extrusion coated tape has then been quenched, re-heated by passing it through a water bath at about 95 °C-98 °C, and oriented at this temperature (with orientation ratios of about 3.6 : 1 in the longitudinal direction and about 3.2 : 1 in the transverse direction) by the trapped-bubble process.

The sequence of layers (from the innermost heat-sealing layer (a') to the outermost abuse layer (b<sup>iv</sup>) in the overall structure is as follows:

(a')/(e')/(f')/(g')/(c)/(d')/(b<sup>iv</sup>)

wherein the resins used for the different layers and, between parentheses, the thickness of each layer are reported below:

(a') heterogeneous ethylene-octene-1 copolymer [ $d = 0.911 \text{ g/cm}^3$  -  $MI = 7 \text{ g/10'}$  (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) - Stamylex 08-076 by DSM] (11  $\mu\text{m}$ )



(e') ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Escorene Ultra FI00014 by Exxon] (6 µm)

(f') ethylene-methacrylic acid copolymer [12 % MA, MI = 1.6 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Nucrel 1202 by DuPont] (6 µm)

5 (g') ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Escorene Ultra FI00014 by Exxon] (6 µm)

(c) a blend of 30 % by weight of vinylidene chloride-methyl acrylate copolymer, 68 % by weight of vinylidene chloride-vinyl chloride and 2 % by weight of epoxidised soybean oil (6 µm)

10 (d') modified VLDPE – Admer AT 1094 E by Mitsui (4 µm)

(b<sup>iv</sup>) a terpolyamide based on polyamide 6, polyamide 11, and polyamide 66 [sold by Bayer under the trade name Durethan® VP KU 2-2153 (m.p. 191 °C)] (6 µm).

#### Example 17

A seven layer film is prepared essentially as described in Example 16 but replacing the resin used for layer (d') with

(d) anhydride grafted and rubber modified LLDPE - Tymor 1203 by Morton.

#### Example 18

A seven-layer film is prepared essentially as described in Example 11 but replacing the resin used for the heat-sealing layer (a) with the following resin

20 (a') heterogeneous ethylene-octene-1 copolymer [ $d = 0.911 \text{ g/cm}^3$  - MI = 7 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Stamylex 08-076 by DSM] and the resin (f) with the following one

(f') ethylene-methacrylic acid copolymer [12 % MA, MI = 1.6 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Nucrel 1202 by DuPont].

#### 25 Example 19

A seven layer film is prepared essentially as described in Example 11 but replacing the resin used for layer (d) with

(d') modified VLDPE – Admer AT 1094 E by Mitsui.

## Example 20

A seven-layer film is prepared essentially as described in Example 19 but replacing the resin used for the outer abuse layer (b''') with

(b'') a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a co-polyamide 6/12 with m.p. = 190 °C ((DSC- 2<sup>nd</sup> heating) [CR-8 by EMS].

## Example 21

A seven-layer film is prepared essentially as described in Example 19 but replacing the resin used for the outer abuse layer (b''') with

(b''') a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a co-polyamide 6/12 with m.p. = 199 °C ((DSC- 2<sup>nd</sup> heating) [CF-85 by EMS].

## Example 22

A seven-layer film is prepared essentially as described in Example 1 but replacing the resin used for the outer abuse layer (b) with

(b<sup>ix</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a co-polyamide 6/66 with m.p. = 196 °C ((DSC- 2<sup>nd</sup> heating) [Ultramid C35 by BASF].

## Example 23

A seven layer film is prepared essentially as described in Example 6 but replacing the resin used for the outer abuse layer (b') with

(b<sup>v</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a co-polyamide 6/66 with m.p. = 196 °C ((DSC- 2<sup>nd</sup> heating) [Ultramid C35 by BASF], and the resin used for intermediate layer (f') with

(f'') heterogeneous ethylene-octene-1 copolymer [ $d = 0.920 \text{ g/cm}^3$  - m.p. = 124 °C (DSC - 2<sup>nd</sup> heating) - MI = 1 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) - Dowlex 2045 E by Dow].

## Example 24

A seven-layer film is prepared essentially as described in Example 16 but replacing the resin used for the outer abuse layer (b<sup>iv</sup>) with

(b<sup>ix</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a terpolyamide based on polyamide 6, polyamide 11, and polyamide 66 [sold by Bayer under the trade name Durethan® VP KU 2-2153 (m.p. 191 °C)]

#### Example 25

A seven layer film is prepared essentially as described in Example 24 but replacing the resin used for layer (f') with

(f'') heterogeneous ethylene-octene-1 copolymer [ $d = 0.920 \text{ g/cm}^3$  - m.p. = 124 °C (DSC - 2<sup>nd</sup> heating) - MI = 1 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) - Dowlex 2045 E by Dow].

#### Example 26

A seven-layer film is prepared essentially as described in Example 24 but replacing the resin used for the outer abuse layer (b<sup>ix</sup>) with

(b<sup>xiii</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of co-polyamide 6/6I with m.p. = 188-190 °C (DSC - 2<sup>nd</sup> heating) [Durethan™ CI31F by Bayer].

#### Example 27

A seven-layer film is prepared by following exactly the same procedure described in Example 11 but avoiding the irradiation step.

#### Example 28

A seven-layer film is prepared by following exactly the same procedure described in Example 17 but reducing the dosage level of the irradiation step to 42 kGy.

#### Example 29

A five layer film is prepared by following the same procedure as in Example 5 but varying the thickness of the gas barrier layer (c) from about 5 µm to about 7 µm, and that of the outer abuse layer (b') from about 5 µm to about 3 µm.

The properties of representative examples of films according to the present invention have been evaluated by submitting the films to the tests indicated below.

% Free shrink : the percent free shrink, i.e. the irreversible and rapid reduction, as a percent, of the original dimensions of a sample subjected to a given temperature under conditions where nil restraint to inhibit shrinkage is present, has been measured according to ASTM D2732, by immersing for 4 seconds specimens of the structures to be tested (10 cm x 10 cm) into a bath of hot water at 90 °C. This attribute has been measured in the longitudinal direction (LD) as well as in the transversal direction (TD) and is reported as the sum thereof, i.e. the total free shrink.

Haze : haze is defined as that percentage of transmitted light which in passing through the specimen deviates from the incident beam by forward scattering, and it has been measured by ASTM D 1003 (Procedure A).

Gloss : the specular gloss of the films, i.e. the relative luminous reflectance factor of a specimen in the mirror direction has been measured using ASTM 2457 - 90 with a gloss angle of 60°.

Modulus : the ratio of the tensile stress to corresponding strain below the proportional limit ( $\text{kg}/\text{cm}^2$ ); measured by ASTM D 882.

Tensile : a measure of the force required at constant elongation to break a specimen of the film ( $\text{kg}/\text{cm}^2$ ); measured by ASTM D 882.

Elongation : a measure of the percent extension required to break a specimen of the film (%); measured by ASTM D 882.

Puncture resistance : the puncture resistance is the resistance force arising when pushing a punch against a surface of flexible film. There is not a standard test method to measure this attribute. The test method used in the present evaluations is described briefly herein below : a film sample (6.5 cm x 6.5 cm) is fixed in a specimen holder connected to a compression cell (1-50 kg normal sensitivity) mounted on a dynamometer (an Instron tensile tester); when the dynamometer is started, a punch (a punching sphere, 5-mm in diameter, soldered on a

plunger) is brought against the film sample at a constant speed (30 cm/min.) and the force needed to puncture the sample is graphically recorded.

In-line abuse resistance : the capability of the tested structures to withstand without breakage the in-line packaging operations, i.e. loading, vacuumizing, sealing, shrinking, and collecting the products through an idle roll conveyor, is defined as "in-line abuse resistance". Scope of this test is to provide a method to discriminate and rank bags of different structure at a laboratory level as to this aspect. The procedure to test this property is therefore devised so as to simulate as much as possible the most drastic conditions that might actually occur in the packaging lines. To perform this test, the bags to be examined are filled with metal blocks, vacuumized, sealed and shrunk on an industrial packaging line. The thus obtained packages are then checked for leakers and the in-line abuse resistance is evaluated by the % of rejects. Due to the harsh conditions purposely employed this number is typically high but, as indicated above, this test has not an absolute but only a relative meaning and its aim is to indicate whether a given structure is expected to have more or less abuse resistance of a standard bag used as comparison, when used at the customer plant.

The % Shrink, Haze, Gloss, Modulus, Tensile and Elongation of some representative structures of the present invention are reported on Table 1.

TABLE 1

Structure of						
20	Example no.	12	13	14	16	17
	% Shrink	72	81	85	89	88
	Haze	2.9	2.9	n.d.	n.d.	n.d.
	Gloss	109	104	n.d.	n.d.	n.d.
	Modulus					
25	LD	3780	4168	n.d.	n.d.	n.d.
	TD	3290	4226	n.d.	n.d.	n.d.
	Tensile					
	LD	930	968	n.d.	n.d.	n.d.

	TD	690	878	n.d.	n.d.	n.d.
Elongation						
	LD	165	200	n.d.	n.d.	n.d.
	TD	117	115	n.d.	n.d.	n.d.

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TABLE 1 continued

Structure of

Example no.	19	24	25	26	28
% Shrink	81	86	75	89	83
Haze	n.d.	3.4	4.3	3.5	n.d.
Gloss	n.d.	93.6	104	94.5	n.d.

The results of the Puncture resistance and In-line abuse resistance tests for some representative structures of the present invention are reported in Table 2 below.

The bags used for the in-line abuse resistance tests were, 165 mm x 230 mm, end sealed bags. For comparative purposes the results obtained with a commercially available bag, 58  $\mu$ m thick, sold by Cryovac® as BB4L, are reported in the last column on the right.

TABLE 2

	Structure of Example no						Cryovac®
	11	12	13	14	17	22	BB4L
Puncture							
(kg) 90°C	1.6	1.8	1.9	1.5	1.5	n.d.	0.5
In-line abuse							
% Rejects	n.d.	28	15	n.d.	n.d.	26	67

TABLE 2 continued

	Structure of Example no					Cryovac®
	23	24	25	26	27	BB4L
Puncture						

(kg) 90°C	n.d.	1.3	1.4	1.3	1.5	0.5
In-line abuse						
% Rejects	41	70	26	74	70	67

n.d.=not determined

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The sealing properties of some representative films of the present invention have been tested by evaluating the seal strength and the integrity of packages obtained by an overlapped sealing. An internal procedure has been developed to evaluate the ability of a heat-shrinkable bag to maintain seal hermeticity and integrity (i.e. no delamination) when submitted to a non-standard sealing cycle. As used herein "non standard sealing cycle" is intended to refer to the case where, in the packaging cycle, the bags filled with the product to be packaged are placed inside a vacuum sealing chamber machine mispositioned (i.e. at least partially overlapped). As indicated above, in an industrial packaging cycle, this may happen, in particular when the positioning of the bags in the vacuum sealing chamber is not controlled by an operator, or this may be done on purpose in order to increase the output per sealing cycle.

This test on overlapped sealability has been carried out on a Cryovac® VSC 75 vacuum sealing machine set with a vacuum time of 20 s, a cooling time of 4 s, a sealing bar pressure of 1 bar and an adjustable impulse time. The test is a comparative test and the results obtained are compared to a standard that is represented by the same bag used however in a standard sealing cycle where the bag is correctly positioned inside the vacuum sealing chamber making sure that no overlap occurs, and the same sealing conditions are applied.

In particular for each formulation two empty end-seal bags (260 mm width) obtained by transverse seal and cut of the oriented tubing, are placed in the center of the sealing bar overlapped one on the other by half of their width in order to simulate a non standard sealing cycle. The shrink bags are vacuumized and sealed at the pre-selected conditions. At the end of the cycle, the two shrink bags are slowly separated, one from the other, by tearing them apart along the seal seam. The seals are then visually checked for seal hermeticity and integrity (no delamination). The tests are then repeated at different impulse sealing times and the range of

impulse times that allows to obtain reliable seals without rejects in case of non standard sealing cycle is determined. In Table 3 below, the minimum sealing impulse time (SIT min.) and the maximum sealing impulse time (SIT max.), i.e. the range of sealing impulse time at which the package hermeticity and integrity characteristics were maintained despite the non standard packaging cycle, are reported for some representative films according to the present invention.

TABLE 3

Structure of Example no.	SIT min. (s)	SIT max (s)
11	1.6	2.4
12	1.6	2.4
13	1.4	2.4
14	1.6	2.4
15	1.6	2.4
22	2.0	2.4
23	2.0	2.4
24	1.6	2.4
25	1.8	2.4
26	1.6	2.0
27	1.6	2.4



## CLAIMS

1. A multi-layer heat-shrinkable film comprising at least  
a first outer heat-sealing layer (a) comprising one or more polyolefins;  
a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175^{\circ}\text{C}$ ; and  
an intermediate gas barrier layer (c) comprising PVDC.
2. The multi-layer heat-shrinkable film of claim 1 wherein the polyamide of the outer abuse layer (b) has a melting point of from about  $175^{\circ}\text{C}$  to about  $250^{\circ}\text{C}$ ; preferably of from about  $180^{\circ}\text{C}$  to about  $240^{\circ}\text{C}$ ; more preferably of from about  $185^{\circ}\text{C}$  to about  $230^{\circ}\text{C}$ ; and still more preferably of from about  $188^{\circ}\text{C}$  to about  $225^{\circ}\text{C}$ .
3. The multi-layer heat-shrinkable film of claim 2 wherein the polyamide of the outer abuse layer (b), with a melting temperature of from about  $188^{\circ}\text{C}$  to about  $225^{\circ}\text{C}$ , is selected from the group consisting of copolyamides 6/12, copolyamides 6/66, polyamide 6 copolymers (modified polyamide 6) comprising less than 5 %, preferably less than 4 %, and even more preferably less than 3 % by weight of an aromatic co-monomer, copolyamides of polyamide 6 and a partially aromatic polyamide, and terpolyamides based on polyamide 6, polyamide 11, and polyamide 66.
4. The multi-layer heat-shrinkable film of claim 2 wherein the outer abuse layer (b) comprises at least 50 % by weight and preferably at least 60 % by weight of one or more polyamides with a m.p.  $\geq 175^{\circ}\text{C}$ , blended with an ethylene-vinyl alcohol copolymer.
5. The multi-layer heat-shrinkable film of claim 4 wherein the amount by weight of EVOH in the outer abuse layer (b) with respect to the overall weight of the layer is comprised between about 3 and about 40 % by weight, preferably between about 5 and about 35 % by weight, and even more preferably between about 10 and about 30 %.
6. The multi-layer heat-shrinkable film of claim 1 wherein the heat-sealing layer (a) comprises a single polyolefin or a blend of two or more polyolefins with melting temperature  $< 140^{\circ}\text{C}$ , preferably  $< 130^{\circ}\text{C}$ , and more preferably comprised between  $80^{\circ}\text{C}$  and about  $128^{\circ}\text{C}$ .

7. The multi-layer heat-shrinkable film of claim 6 wherein the heat-sealing layer (a) comprises heterogeneous or homogeneous ethylene-(C<sub>4</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymers having a density  $\leq 0.915$  g/cm<sup>3</sup>, blends thereof with minor amount of polyethylene homopolymers, ethylene-vinyl acetate copolymers, ethylene-acrylic or methacrylic acid copolymers including ionomers, blends of heterogeneous or homogeneous ethylene-(C<sub>4</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymers having a density from about 0.915 g/cm<sup>3</sup> to about 0.930 g/cm<sup>3</sup> with ethylene-vinyl-acetate copolymers or ethylene-alkyl (meth)acrylate copolymers, ethylene-propylene-butene ter-polymers, ethylene-alkyl acrylate-maleic anhydride ter-polymers.
8. The multi-layer heat-shrinkable film of claim 7 wherein the heat-sealing layer (a) comprises a heterogeneous or homogeneous ethylene-(C<sub>4</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymer having a density  $\leq 0.915$  g/cm<sup>3</sup>, and preferably a heterogeneous or homogeneous ethylene-(C<sub>4</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymer having a density comprised between about 0.895 g/cm<sup>3</sup> and about 0.912 g/cm<sup>3</sup>.
9. The multi-layer heat-shrinkable film of claim 1 in the form of a seamless tubing wherein the outer heat-sealing layer (a) is the innermost layer of the tube.
10. A container obtained from a multi-layer heat-shrinkable film comprising at least
  - a first outer heat-sealing layer (a) comprising one or more polyolefins;
  - a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and
  - an intermediate gas barrier layer (c) comprising PVDC,
 by a welding involving the outer heat-sealing layer (a), whereby said outer layer (a) is the inside layer of the container and the outer abuse layer (b) is the outside layer of the container.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Paleari et al                      Docket No.: D-42992-01  
PCT App. No. PCT/EP99/07941              Group Art No.:  
Serial No.: 09/807,210                      Examiner:  
Filing Date: 04-10-01  
Title: NEW HIGH RESISTANCE HEAT SHRINKABLE THERMOPLASTIC FILM

COMBINED DECLARATION AND POWER OF ATTORNEY

Sir:

As the above-identified inventors, we hereby declare that:

- 1) Our residence and post office addresses and citizenship are given below.
- 2) We believe that we are the first, joint, and original inventors of the subject matter which is claimed and for which a patent is sought for the above-entitled invention, the specification of which was filed on April 10, 2001 under application number 09/807,210.
- 3) We have reviewed and understand the contents of the above-identified specification, including the claims and any drawings attached thereto.
- 4) We acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations 1.56(a).
- 5) Pursuant to 35 U.S.C. 119, we hereby claim foreign priority benefits based upon the below-identified foreign applications for patent or inventor's certificate:

Country: PCT  
International App. No.: PCT/EP99/07941  
International Filing Date: 10-19-99

6) We hereby appoint the following attorneys who may be reached at the below-identified address and telephone numbers, to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith: John J. Wasatonic, Registration No. 29,984, Mark B. Quatt, Registration No. 30,484; Rupert B. Hurley Jr., Registration No. 29,313, Thomas C. Lagaly, Registration No. 34,652 and Daniel B. Ruble, Registration No. 40,794.

Direct all correspondence and telephone calls to Mark B. Quatt at:

Address: Cryovac, Inc.  
P. O. Box 464  
Duncan, SC 29334  
Telephone: (864) 433-2817

7) All statements made herein of our own knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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